



# Study on recognition and separation of rare earth ions at picometre scale by using efficient ion-surface imprinted polymer materials



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## ABSTRACT

The graft-polymerization of hydroxyethyl methacrylate (HEMA) on micro-sized silica gel particles was first conducted by initiating of a surface-initiating system, which was constituted by the bonded amino groups on the modified silica gel particles and persulfate in the solution, obtaining the grafted particles PHEMA/SiO<sub>2</sub> with a high grafting degree of 40 g/100 g. Subsequently, 8-hydroxyquinoline as a ligand with strong chelating ability for metal ions was bonded on the side chains of the grafted macromolecule PHEMA through the substitution reaction between 5-chloromethyl-8-hydroxyquinoline (CHQ) and the hydroxyl group of the grafted macromolecule PHEMA, preparing the functional grafted particles HQ-PHEMA/SiO<sub>2</sub>. On the basis of examining the chelating adsorption property of HQ-PHEMA/SiO<sub>2</sub> particles for Pr<sup>3+</sup> ion, the Pr<sup>3+</sup> ion surface-imprinting was carried out by using the effective surface-imprinting technique of “pre-grafting and post-crosslinking/imprinting” established by our group. During the surface-imprinting process, Pr<sup>3+</sup> ion was used as a template ion, and 2,2'-dichlorodiethyl ether was used crosslinked, resulting in the Pr<sup>3+</sup> ion surface-imprinted material IIP-HQP/SiO<sub>2</sub>. The recognition and binding characters of IIP-HQP/SiO<sub>2</sub> towards Pr<sup>3+</sup> ion were investigated in-depth with La<sup>3+</sup> and Ce<sup>3+</sup> ions as two contrast ions. The experimental results show that the IIP-HQP/SiO<sub>2</sub> particles possess special recognition selectivity and high binding ability for Pr<sup>3+</sup> ion. The binding capacity of IIP-HQP/SiO<sub>2</sub> for Pr<sup>3+</sup> ion reaches 0.13 mmol/g, and relative to La<sup>3+</sup> and Ce<sup>3+</sup> ions, the selectivity coefficients of IIP-HQP/SiO<sub>2</sub> for Pr<sup>3+</sup> ion are 5.22 and 5.12, respectively. La, Ce and Pr are three neighbouring rare earth elements, and the ion radius differences between La<sup>3+</sup>, Ce<sup>3+</sup> and Pr<sup>3+</sup> ions are only in a range of 2–5 pm. Obviously, in this investigation, the mutual separation of La<sup>3+</sup>, Ce<sup>3+</sup> and Pr<sup>3+</sup> ions at picometre scale is realized successfully by using the ion surface-imprinted polymer material with high performance.

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## 1. Introduction

Rare earth (RE) elements are a very important group of chemical elements. Owing to their peculiar physical, chemical, and nuclear properties of themselves or their compounds, the RE elements play an important role in many fields of advanced materials science such as electronics, magnetism, metallurgy, phosphors, catalysts, glass, laser and ceramic technology (Abreu and Morais, 2010; Hasegawa et al., 2011; Jia et al., 2009; Jordens et al., 2013; Lee et al., 2010). The rare earth elements invariably occur together in the source minerals (bastansite, monazite, and xenotime) (Banda et al., 2012; Nasab et al., 2011). The rare earth elements are required to be mutually separated for the industrial applications. Further, the purification of these elements is gaining considerable attention with the ever-increasing demand for high-purity rare earth elements and their compounds. However, the separation and recovery of rare earths are very difficult

because of the similarity of their chemical properties derived from their same valence and similar ion radii (arising from lanthanide contraction) (Suzuki et al., 2006; Wannachod et al., 2011), especially for the separation of those light rare earths from each other. The selective separation of mixed rare-earth (RE) metals poses glaring challenge to the industry. The separation methods are variously conducted, but there are the two basic types, solvent extraction and ion exchange technologies (Belova et al., 2009; Hubicka and Kołodyńska, 2008; Lee et al., 2009). In both conventional separation methods, there are some problems, such as complicated operation, lack of selectivity, tight separability condition, remain of organic material, and restriction on separable rare earth elements (Lee et al., 2009; Suzuki et al., 2006). Therefore, it is needed to develop new methods and materials for facilitating the separation and purification of rare earth elements.

In the present work, we propose a more simple and highly effective separation technique based on the rare earth ion surface-imprinted material, and try to conduct the separation of the three neighbouring light rare earth ions, lanthanum (La<sup>3+</sup>), cerium (Ce<sup>3+</sup>) and praseodymium (Pr<sup>3+</sup>) ions, so as to realize their mutual separation at picometre scale (the difference of their ionic radii is in a range of 2–5 pm).

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Molecular imprinting is a technique for creating polymeric matrices containing tailor-made receptors and having special recognition ability and predesigned selectivity for the template molecule (Athikomrattanakul et al., 2009; Okutucu and Önal, 2011; Qi et al., 2010), and so molecularly imprinted polymers (MIPs) are described as artificial antibodies or receptors. Within the particles of MIPs, a great deal of imprinted cavities is distributed and these cavities are complementary to the template molecule in shape, size and functionality, and it is the fundamental reason that MIPs have the special recognition selectivity for the template molecule. As the template is an ion in the preparation process of MIPs, the resultant products are called ion-imprinted polymers (IIPs) that especially recognize the template ion (Otero-Romaní et al., 2009; Vatanpour et al., 2011). In recent years, the molecular imprinting solid-phase extraction (MISPE) technique with MIPs as well as IIPs as solid adsorbents with high performance has been widely used in many fields, in which the fine selectivity for the target substances is required, such as separation, purification, pre-concentration and determining, and constructing sensors (Akdamar et al., 2009; Byun et al., 2010; Javanbakht et al., 2009; Patel et al., 2009; Yuan et al., 2011). We think that introducing ion-imprinting technique into hydrometallurgy is promising, and it is potential to use MIPSPE method with IIPs as solid adsorbents for separating the neighbouring rare earth elements.

The conventional method of preparing molecular imprinted polymers (MIPs) is entrapment way, and the prepared MIPs have some disadvantages (Kitahara et al., 2010; Pan et al., 2011), such as taking time, complicated preparation process, less recognition sites inside the matrix particle obtained by crushing and grinding the imprinted polymeric monolith, and greater diffusion resistance for the template molecules because of the thick matrix. These shortcomings make MIPs prepared with the conventional method to have poor binding property and slow binding kinetics for the template molecules. In order to overcome these drawbacks, recently, the various surface-imprinting methods have been actively developed (Gai et al., 2011; Gu et al., 2011; Wang et al., 2008), and the researchers try to build molecular recognition systems on the surface of solid particles. We also devote ourselves to develop the new surface-imprinting methods. Lately, we put forward a novel molecule (ion) surface-imprinting technique of “pre-grafting and post-crosslinking/imprinting” (Gao et al., 2009; Gao et al., 2010; Gao et al., 2011; Gao et al., 2013a, 2013b). Its basic points are as follows. Functional polymers, which has strong adsorption action for the template molecule or ion, are pre-grafted on the surfaces of micron-sized solid particles, and subsequently, the post-crosslinking of the functional polymers, which has adsorbed the template molecule or ion, is conducted using special crosslinking agent so as to realize the imprinting of the template molecule or ion. After the removal of the template molecules, a mass of the imprinted caves capable of recognizing and re-binding the template molecules (ions) is left and distributed within a thin polymer layer on the surfaces of the solid particles, resulting in the surface-imprinted material with high performance. Using the surface imprinting described above, we prepared various molecule or ion imprinted materials, and the prepared surface-imprinted materials have excellent recognition selectivity and high binding capacity for the template molecule or ion as well as exhibit fast mass transfer rate.

In the prior research of ours (Fang et al., 2012), by using a surface-initiated graft-polymerization method, hydroxyethyl methacrylate (HEMA) was first graft-polymerized onto the surfaces of micro-sized silica gel particles, obtaining the grafted particles PHEMA/SiO<sub>2</sub>, and then 8-hydroxyquinoline (HQ) as a ligand with strong chelating ability for metal ions was bonded on the side chain of the grafted macromolecule PHEMA, obtaining the functional grafted particles HQ-PHEMA/SiO<sub>2</sub>. In this work, HQ-PHEMA was used as functional polymer, on which the bonded HQ could strongly coordinate to rare earth ion as well as other transition metal ions, and on this basis, the Pr<sup>3+</sup> ion surface-imprinting was carried out successfully on the surfaces of HQ-PHEMA/

SiO<sub>2</sub> particles by using the novel ion surface-imprinting technique of “pre-grafting and post-crosslinking/imprinting”, getting Pr<sup>3+</sup> ion surface-imprinted material IIP-HQP/SiO<sub>2</sub>. The ion recognition and separation property of IIP-HQP/SiO<sub>2</sub> for three neighbouring light rare earth element ions, La<sup>3+</sup>, Ce<sup>3+</sup> and Pr<sup>3+</sup> ions, were investigated in-depth. The imprinted material IIP-HQP/SiO<sub>2</sub> has special recognition selectivity for Pr<sup>3+</sup> ion, and can separate these neighbouring light rare earth element ions at picometre scale. It is obvious that such investigation is significant in hydrometallurgy as well as in the purification of rare earth elements, and it is reported for the first time.

## 2. Experimental section

### 2.1. Materials and instruments

Silica (about 125 μm of diameter, Ocean Chemical Limited Company, Qingdao City, China) was of reagent grade. γ-Aminopropyltrimethoxysilane (AMPS, Nanking Chuangshi Chemical Aux Ltd., Jiangsu Province, China) was of analytical grade. Hydroxyethyl methacrylate (HEMA, Tianjin Institute of Chemical Reagents, Tianjin City, China) was of analytical grade, and was purified via vacuum distillation before use. Ammonium persulfate (APS, Tianjin Damao Chemical Reagent Plant, Tianjin City, China) was of analytical grade. 5-Chloromethyl-8-hydroxyquinoline (CHQ) was self-prepared (Gao et al., 2013a, 2013b). 2,2'-Dichlorodiethyl ether (Wuxi Fanrong Supplies Co. Ltd., Jiangsu Province). *N,N*-dimethyl formamide (DMF, Tientsin University Chemical Reagent Plant, Tientsin City, China) was of analytical grade. Lanthanum nitrate and cerium nitrate (Tianjin Damao Chemical Reagent Plant, Tianjin City, China) were of analytical grade. Praseodymium oxide (Pr<sub>2</sub>O<sub>3</sub>) was supplied by Beijing General Research Institute for Nonferrous Metals. Other reagents were all commercial chemicals with analytical pure grade and purchased from Chinese companies.

The instruments used in this study were as follows: Perkin-Elmer 1700 infrared spectrometer (Perkin-Elmer Company, USA); LEO-438VP scanning electronic microscope (SEM, LEO Company, UK), STA449 thermogravimetry analyzer (TGA, Netzsch Company, Germany); PHS-3C pH meter (Shanghai Precision Scientific Apparatus Inc., Shanghai, China); THZ-92C constant temperature shaker equipped with water bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai, China); Unic-2602 UV/vis spectrophotometer (Unic Company, Shanghai).

### 2.2. Preparation and characterization of functional particles HQ-PHEMA/SiO<sub>2</sub>

According to the procedure described by Fang et al. (2012), the functional particles HQ-PHEMA/SiO<sub>2</sub> were prepared through two sets of partial reactions, graft-polymerization of PHEMA and functionalization transforming of the grafted particles. (1) The graft-polymerization of HEMA on the surfaces of silica gel particles was effectively carried out with a surface-initiated graft-polymerization method, and the process is briefly stated as follows. The micro-sized silica gel particles were surface-modified with coupling agent AMPS to introduce amino groups onto the surfaces of silica gel particles, getting the surface-modified particles AMPS-SiO<sub>2</sub>. (2) A redox initiating system was constituted by the amino group on SiO<sub>2</sub> and the APS in the solution of DMF, and the surface-initiated graft-polymerization of HEMA was conducted under N<sub>2</sub> atmosphere, obtaining the grafted particles PHEMA/SiO<sub>2</sub> with a high grafting degree (40 g/100 g). The grafted particles PHEMA/SiO<sub>2</sub> were fully characterized by using several means, such as FTIR, SEM and TGA (Fang et al., 2012). (3) The HQ-functionalization transforming of the grafted particles PHEMA/SiO<sub>2</sub> was realized through the nucleophilic substitution reaction between CHQ and the side hydroxyl groups of the grafted macromolecules PHEMA. The substitution reaction was conducted at 90 °C and under N<sub>2</sub> atmosphere for 7 h with Na<sub>2</sub>CO<sub>3</sub> as acid acceptor, preparing the functional grafted particles HQ-PHEMA/SiO<sub>2</sub>. The infrared spectrum of HQ-PHEMA/SiO<sub>2</sub> particles were determined with

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